Theoretical Investigation of the Structure and Coverage of the Si(111)-OCH_3 Surface

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Supporting Information

1. Pseudopotentials and basis sets

The pseudopotentials used in these calculations are standard norm-conserving, non-separable pseudopotentials[1] generated using Hamann's methods[2,3] (the generalized norm-conserving pseudopotential method[2] was used for iodine and the new method[3] for all other atoms). The carbon, oxygen, silicon and iodine pseudopotentials included up to l=1, l=2, l=2 and l=3 projectors, respectively (with standard settings), with the l=1, l=2, l=2 and l=3 potentials, respectively, used as the local potential in each case. The hydrogen atom was also treated as a pseudopotential (rather than with a bare-core potential), with only an l=0 potential.

Multiple tests with hydrogen atoms, H_2 molecules and water molecules verified that the energetics of the bare core hydrogen potential and the hydrogen pseudopotential are almost indistinguishable.

The basis functions were double-zeta plus polarization quality, formed from contracted Gaussians. Hence the *occupied* orbitals Si-*s* and Si-*p*, and the H-*s*, for example, had two radial degrees of freedom, and the Si-*d* and H-*p unoccupied* angular polarization orbitals had only one. The basis sets for hydrogen, carbon, oxygen, silicon, and iodine were contracted (4s1p/2s1p), (5s4p1d/2s2p1d), (5s5p2d/2s2p1d), (4s3p1d/2s2p1d) and (5s5p1d/2s2p1d) basis sets, respectively. This nomenclature denotes, for H for example, that four Gaussian *s*-functions were contracted into two independent functions, and one Gaussian *p*-function was used as one independent radial degree of freedom. The *d*-functions (for carbon, oxygen, silicon and iodine) were made up of the five pure *l*=2 functions, i.e., the *s*-combination was excluded. The Gaussians and contraction coefficients for hydrogen, carbon, oxygen, silicon and iodine are listed in Tables S-1, S-2, S-3, S-4 and S-5.

Table S-1: *Basis set for hydrogen. The Gaussian decay constants α (1/bohr^2), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).*

s-functions			**p-function**	
α_s	c_α (1st zeta)	c_α (2nd zeta)	α_p	c_α
0.102474	0.087388	0.075281	1.100000	1.000000
0.372304	0.405344	0.120939		
1.230858	0.485455	0		
4.783324	0.397563	0		

Table S-2: *Basis set for carbon. The Gaussian decay constants α (1/bohr^2), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).*

s-functions			**p-functions**			**d-function**	
α_s	C_α (1st zeta)	c_α (2nd zeta)	α_p	c_α (1st zeta)	c_α (2nd zeta)	α_d	c_α
0.155830	0.219500	1.000000	0.154701	0.107631	1.000000	0.770000	1.000000
0.458320	0.695623	0	0.523908	0.524630	0		
1.40253	0.362537	0	1.442267	1.002503	0		
2.805200	-1.296428	0	4.604695	1.675411	0		
5.610400	0.450261	0					

Table S-3: *Basis set for oxygen. The Gaussian decay constants α (1/bohr^2), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).*

s-functions			**p-functions**			**d-function**	
α_s	C_α (1st zeta)	C_α (2nd zeta)	α_p	c_α (1st zeta	c_α (2nd zeta)	α_d	c_α
0.193491	0.171240	1.000000	0.132619	0.059909	0.386000	0.220000	0.077290
0.521475	0.875614	0	0.392437	0.313640	1.000000	1.1000000	1.000000
1.426025	1.340022	0	1.057896	1.189398	0		
2.852050	-1.216661	0	3.145166	3.676785	0		
5.70410	0.321921	0	6.769595	-0.683244	0		

Table S-4: *Basis set for silicon. The Gaussian decay constants α (1/bohr^2), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).*

s-functions			**p-functions**			**d-function**	
α_s	c_α (1st zeta)	c_α (2nd zeta)	α_p	c_α (1st zeta)	c_α (2nd zeta)	α_d	c_α
0.104600	0.209953	1.0	0.094241	0.067616	1.0	0.450000	1.000000
0.272263	0.559782	0	0.317679	0.318212	0		
1.300508	-0.991282	0	1.561145	-0.066383	0		
2.601030	0.334871	0					

Table S-5: *Basis set for iodine. The Gaussian decay constants α (1/bohr^2), and associated contraction coefficients c_α for the contracted Gaussian basis functions (unnormalized).*

s-functions			**p-functions**			**d-function**	
α_s	c_α (1st zeta)	c_α (2nd zeta)	α_p	c_α (1st zeta)	c_α (2nd zeta)	α_d	c_α
0.1266970	0.241525	1.000000	0.082022	0.041662	1.000000	0.270000	1.000000
0.3143620	0.880824	0	0.218520	0.253357	0		
1.407096	-2.139824	0	0.508736	0.375408	0		
2.814300	1.495950	0	1.181286	-0.720357	0		
5.628600	-0.387679	0	2.362700	0.246727	0		

2. K-points

The number of k-points for each calculation was varied according to the unit cell size. 8 k-points were used in the direction of each of the two cell unit vectors for the 1x1 unit cell (there are only two unit vectors because the models used are only 2D periodic). The number of k-points for the other structures was set to the closest integer, inversely proportional to the cell dimension along each unit vector. Thus, the 2x2 and 3x3 unit cells had 4 and 3 k-points in each direction, respectively.

3. Spin polarization

Calculations of singlet states were performed with restricted (closed shell) DFT. Calculations of doublet (radical) states or dissociated triplet states, necessary for the computation of bond energies, were performed with unrestricted (spin-polarized) DFT, in which the N_α spin-up and N_β spin-down orbitals were optimized independently.

4. References

1. A. Redondo, W.A. Goddard III and T.C. McGill, Phys. Rev. B 15, 5038 (1977)

2. D.R. Hamann, Phys. Rev. 40, 2980 (1989)

3. D.R. Hamann, pseudopotential generation program PUNSLDX, unpublished.